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A STUDY OF THE FUNDAMENTALS
OF LIQUID PROPELLANT SENSITIVITY

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FOREWORD

This is Report No. IITRI C-6024-8, the second
Technical Progress Report on C6024, Contract No. AF 04(611)-9566,
entitled "A Study of the Fundamentals of Liquid Propellant
Sensitivity."

Mr. Ted A. Erikson, Research Engineer, is   project
leader. Other IITRI personnel who contributed to the research
effort during this quarter include: Dr. Morton J. Klein,
Assistant Director of Chemistry Research; Mr. Charles K. Hersh,
Manager of Propellant Research; Mr. Theodore Burgwald, Research
Chemist; Mr. Allen J. Tulis, Associate Engineer; and Mr. Odis
Flynn, Technician.

Data for this project are recorded in IITRI Logbooks
C14196 and C14197.

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ABSTRACT

Preliminary sensitivity tests of lead azide samples, with initial temperatures to -170°C, have been performed in the new cryogenic IITRI shock-tube facility. Detonations were generally identified within 200 microseconds of the time that incident Mach 2.6 nitrogen shocks were reflected from the surface of the sample. Two characteristic induction periods were noted. The first period can be considered typical. The second period exhibited an increasing light output which stabilizes. Subsequent light output jumps instantaneously and work output follows within 10-30 microseconds.

An appreciable sensitivity increase was identified with traces of air (oxygen) in the driven gas and lowered initial azide sample temperatures of 200°C; at otherwise constant conditions time delays decreased by factors of 10 and 2, respectively.

Shock-tube tests of C-N-F compounds will follow the check out of equipment and instrumentation that is being performed with the lead azide.

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A STUDY OF THE FUNDAMENTALS OF LIQUID PROPELLANT SENSITIVITY

I.   INTRODUCTION

In this program, the approach to propellant desensitization is based on an evaluation of the various parameters which affect the initiation, growth, and propagation of explosive liquid systems. Shock-tube testing is being used as a primary experimental tool for evaluation of parameters. Specific parameters to be studied are temperature, pressure, and composition of the gas in (practically) instantaneous contact with the surface of the condensed phase. Flash irradiation will be used as a supplementary test when feasible.

The standard IITRI shock tube has been cryogenically modified for the sensitivity testing of C-N-F compounds. The testing procedure has been evaluated by using lead azide as an explosive system at room temperature and at cryogenic temperatures down to -170°C. The equipment for the chromatographic purification of C-N-F compounds (supplied to IIT Research Institute by other laboratories) has been collected, and assembly is in process.

II.   STATUS OF RESEARCH

A.   Cryogenic Shock Tube

The design of the cryogenic shock-tube sensitivity-testing device was described in the last Technical Status Report. A minor modification was made after the preliminary tests. Explosions distorted the sample-site area and, in addition, the copper bar (used as the sample site and a heat pump) was eventually blown out of the holder. Replaceable sample-site inserts have been made to screw onto the end of the copper bar, and a collar was positioned so it would prevent movement due to the explosive force. Details of these modifications are shown in the Appendix. No other changes are planned at this time, since operation of the equipment and instrumentation has otherwise been very satisfactory (Figure 1).
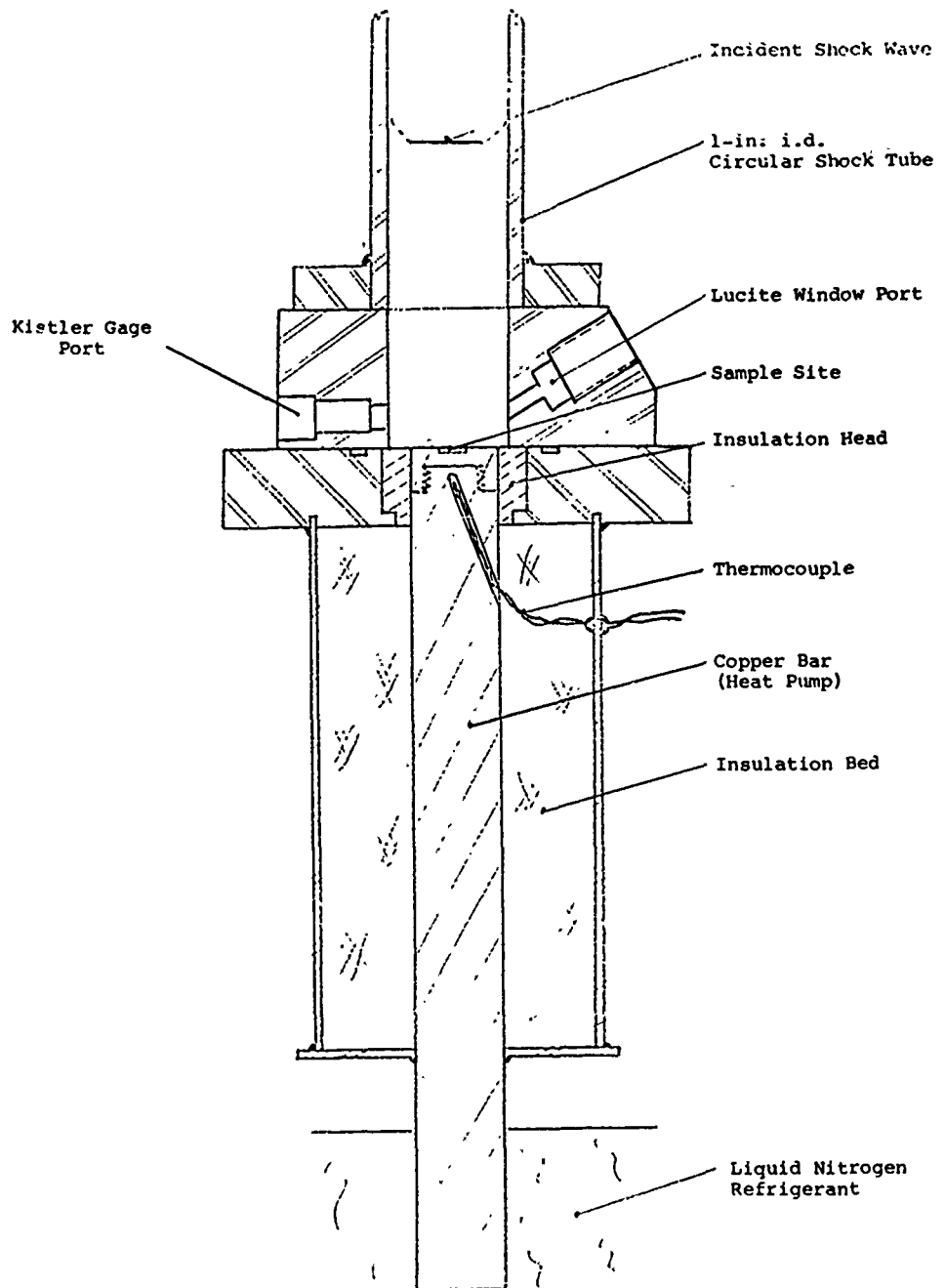
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Figure 1

SAMPLE TEST AREA IN NEW CRYOGENIC ADAPTATION
OF THE IITRI SHOCK TUBE

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A Kistler PZ-6 miniature pressure transducer monitors the incident and the reflected shock pressures. A unique use of this gage is to detect the moment of detonation by a characteristic reverberation (ring) signal that is transmitted through the end plate and up the wall of the shock tube. The light-detection device is a Texas Instrument IS-400 silicon planar phototransistor. The sensor is normally powered through a load resistance of 100,000 ohms with 4.05 volts of direct current supplied by 3 mercury cells. The time resolution of the instrumentation circuits are estimated at better than 5 and 1 microseconds for the Kistler gage and the light sensor, respectively.

B.   Testing

1.   Preliminary Results:

Preliminary testing is being performed to establish an operation procedure at room temperature and at cryogenic temperatures. The use of the instrumentation to simultaneously monitor light and work (detonation) output must also be thoroughly established. The C-N-F compounds have limited availability and thus cannot be used for checkout procedures.

Tests were conducted with colloidal lead azide specially prepared by the Picatinny Arsenal (ref. 1). Impurities were reported at less than 0.1%; the average particle size was 6 microns; and the average density was 4.52 g/cc. Azide samples in a water solution were deposited on the sample site with a medicine dropper (Figure 1). The shock tube was then closed and evacuated for about 30 minutes to remove the water. The final dry sample weight was estimated at 0.05 g.

In early tests, the driven section pressure (after evacuation) was adjusted to 3.8 psia with nitrogen gas. In later tests, the system was brought above atmospheric pressure, flushed for about 10 minutes, and adjusted to 15 psia with pure nitrogen gas. This technique was introduced in order to eliminate any trace of air or oxygen, regardless of whether a minor leak was present. It was found in the early testing that minute amounts of air (oxygen) caused the light sensor to exhibit an appreciable output of light. This is believed to be due to either luminosity of the heated oxygen gas or small combustion pockets at the surface of the Lucite window. In any event, this problem is being avoided by performing experiments with pure nitrogen as the driven gas.

Photographic records of representative oscilloscope traces are shown in Figure 2. The sweep is triggered by the initial pressure rise as the incident shock passes across the face of the Kistler gage. Pressure output increases upward from the lower horizontal hatched line on the photographs and the light output increases downward from the upper line Blank shocks are also exhibited for comparison and orientation of the signal outputs. The conditions for these and other pertinent tests are summarized in Table 1.

Table 1 indicates the initial sample temperature, the driver gas pressure (helium), the driver- to driven-gas pressure ratio, and the incident shock Mach number. The reverberation signal of the Kistler gage is almost always preceded by a small amount of light output and then a large amount of light output (saturation of sensor at 4 volts). These times are identified as t_d, t_+, and t_{++}, respectively, in Table 1. Shocks at approximately Mach 3.6 and 2.6 were generated; the results from the latter are expected to be more reliable because of the above-mentioned technique to positively eliminate air or oxygen.

In general, the results indicate that a shorter time delay occurs with the stronger Mach shock of 3.6 relative to the conditions used to generate the 2.6 Mach shock. It appears that the presence of air (or oxygen) strongly sensitizes the initiation of lead azide, indicated by time delays over 400% or more when leaks are not suspected.

In the more reliable Mach 2.6 nitrogen shock test, an output of limited light occurs approximately 100 μ-seconds after reception of the incident shock wave at the surface of the sample. A nearly constant light output of about 1/2 volt continues for about another 100 μ-seconds and sharply increased light intensity saturates the photocell almost instantaneously. No less than 10 μ-seconds (believed to be more than instrumentation response) elapses before a detonation is identified by the reverberation signal received at the Kistler gage. The time for the reverberation signal to pass through the end plate and up the shock-tube wall to the Kistler gage site was estimated to be less than 3 μ-seconds.

In any event, the time for the first appearance of light appears to be the more reproducible, and the induction or transition times for the appearance of a large amount of light and detonation work output are more sporadic. The former value was calculated as 106 $\pm$ 6 -seconds, and the latter varied in the ranges of 110 to 220 and 10 to 30 μ-seconds for the series of 6 tests at room temperature (Table 1).
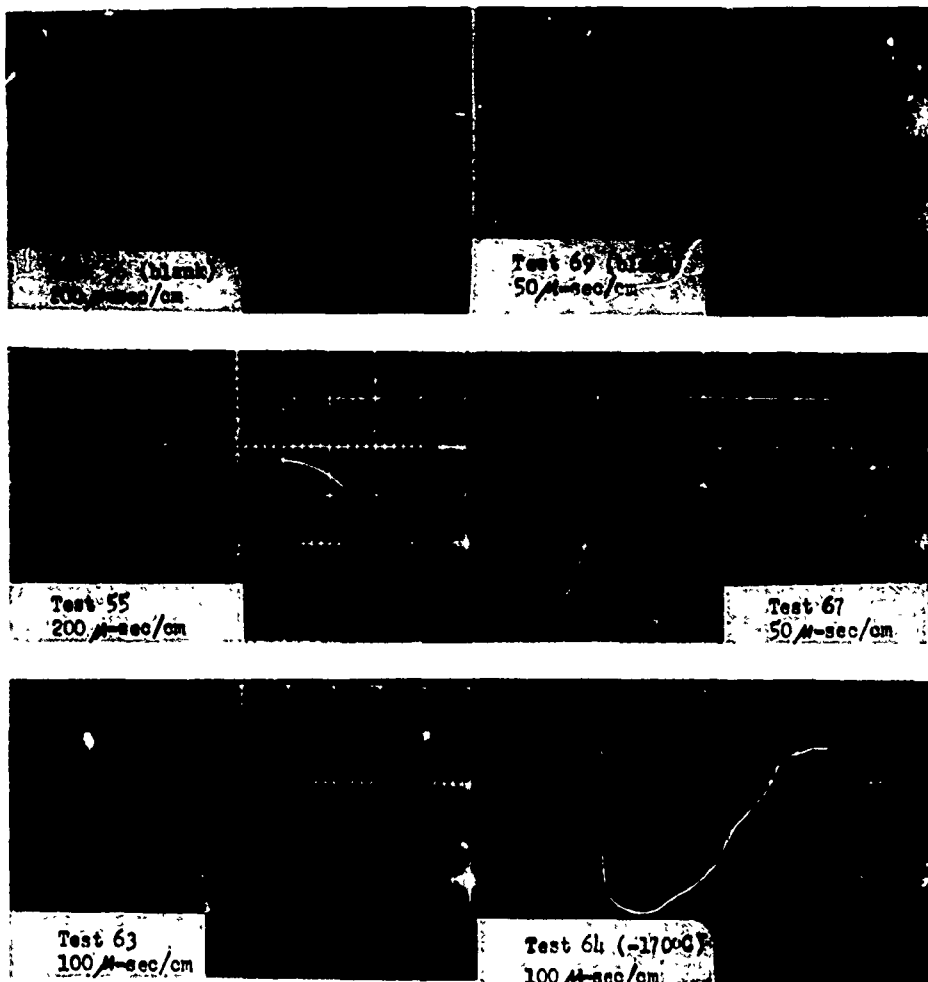
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Figure 2

REPRESENTATIVE OSCILLOSCOPE TRACES
FOR SHOCK-TUBE TESTS WITH LEAD AZIDE
(Initial sample temperature is 25 °C
unless indicated otherwise – See Table 1
and Text)

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Table 1

LEAD AZIDE TESTS IN IITRI SHOCK TUBE[*]

Test No.	Sample Temp., °C	Driver Pressure, psia N	Driver- to Driven-Gas Pressure Ratio	Incident Mach No.	Time, microseconds[**]		
					t_+	t_{++}	t_D
13	25	3.80	59.3	3.6	50	360	750
15	25	3.80	57.8	3.6	40	160	180
17	25	3.80 air?	62.0	3.6	about	20	20
19	25	3.80 air?	62.0	3.6	about	20	20
40	25	3.80	56.6	3.6	60	80	130
44	25	3.80 air?	57.0	3.6	about	30	30
45	-170	3.80 air?	57.0	3.6	about	30	50
51	25	3.80 air?	57.0	3.6	about	20	20
55	25	15	15.	2.6	100	200	210
58	25	15	15.	2.6	100	160	200
61	-170	15	15.	2.6	None	80	100
63	25	15	15.	2.6	140	250	270
64	-170	15	15.	2.6	None	160	170
67	25	14.6	16.1	2.6	110	250	260
68	25	14.6	16.1	2.6	110	330	350
70	25	14.6	16.1	2.6	80	160	190

[*]Tests to establish testing and cryogenic procedures.

[**]Induction time from shock reflection at sample surface to appearance of a small amount of light, t_+; a large amount of light, t_{++}; and work output due to detonation, t_D.

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Decreasing the sample temperature to -170°C before the shock-tube test (1) decreased the time delay by about 50% and (2) extinguished the small amount of light output in the two successful tests. Further tests are needed to establish the reliability of these results and to establish the procedure of subjecting a material to a 200°C-thermal shock before testing.

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2. Discussion of Results

The results to date have positively identified at least two important features of the explosive initiation process for lead azide subjected to the IITRI shock-tube test. First, various light levels precede the output of work which results because of the establishment of a detonation. Second, the initial character of light output is low and remains relatively constant for a long induction period, and then almost instantaneously jumps to a very high level just before detonation. Less reliable evidence (insufficient tests) indicate (1) an increased sensitivity when small amounts of air or oxygen are present, and (2) an increased sensitivity when a negative 200°C thermal shock is imposed on the system before the test.

The results are all unique since, to our knowledge, no effort has ever been made to identify the character of both light and work output or lowered temperature with a sensitivity test. In general, most tests tend to smear the results because of concurrent processes. The IITRI shock-tube test exposes the surface of the condensed phase to the hot, pressurized gas, produced by reflection of an incident shock wave with minimum disturbance to the sample and the gas. Transmitted shocks bear such a small magnitude that they are negligible. Energy transfer from the gas to the condensed phase is the only way ignition can be affected. Since this process approximates the way that an explosion must be sustained during propagation, it is believed that this technique is better able to thumbprint sensitivity. Complications must occur because the sensitivity is probably related to the effect that pressure, temperature, and composition of the driven gas have on the induction periods or time delays that are measured. Prior experience (ref 1-3) has shown that the induction time to work output, measured by the reverberation pickup of the Kistler gage, was influenced by these variables. This program indicates at least one, and possibly two, more induction periods associated with a small amount and a large amount of light output. Thus pressure, temperature and composition of the driven gas in contact with the surface may independently influence at least two induction periods.

Some discussion of the meaning of the results obtained is in order, although with reservations. An exothermic reaction near the surface of the condensed phase would be expected to increase the light level as the usual cascade of heat accumulation and temperature rise progress. Actually, the light level rises quickly after an initial induction period and levels off for another successive induction period. This evidence seems to indicate that at least two processes are present: an initial reaction of exothermic character which causes heating

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(emission) and a later competing reaction of probable
endothermic character which absorbs the heat from the first
reaction. Thus, an induction period ensues wherein two
competing reactions equalize their reaction heats as their
reaction rates increase. A change-of-reaction mechanism
must then occur in which the process makes a deflagration-
to-detonation transition as high level light output appears.
Even here, there is evidence of a lag, which may again
indicate two competing reactions before a high-order detonation
is established.

In any event, the key to sensitivity and desensitization
must lie in the identification of the reaction elements that
are required for a detonation. The effects of the pressure,
temperature, and composition of the driven gas can all be
used to help identify the reaction types that must be
initiated.

For example, Bowden (ref. 4) discusses the mechanism for
the decomposition of azides by both heat and light. Basically,
it is suggested that electrons must be excited by heat or
light in order to jump from the valence to the conduction band.
This energy gap is related to the activation energies that are
obtained in experiments on thermal and photochemical
decomposition. In thermal decomposition, the first stage is the
formation of a positive hole, that is, an electron deficiency
in the valence band and the transfer of an electron to the
conduction band.

$$N_3^- = N_3 + e \qquad\qquad (1)$$

In photochemical decomposition with light of wavelength
corresponding to high absorption coefficients (or excitation
bands), it is proposed that the azide ion divides in the
following manner.

$$N_3^- + h\nu = N_3 + e \qquad\qquad (2)$$
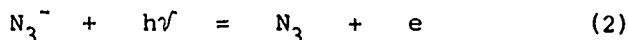
Thus, it is not inconceivable that one reaction predominates
at one stage in the explosive process, and the other predominates
at a later stage. Reaction 2 is most likely to occur during
the detonation of lead azide in shock-tube examination,
since high output of light is indicated by the light sensor.

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C. Sample Purification

A gas chromatographic unit for the separation and the purification of compounds to be tested on this program is currently being constructed. The following pieces of equipment have been procured by IITRI and are being incorporated into the final design:

1. Gas chromatograph -- Nester Faust Anakro 1A, four-element hot-wire detector, integral pyrometer, variable preheater, column and cell to 500°C.

2. Recorder -- Dynatronic Instruments Corp. Graphicorder Model No. 8020, rectilinear recording, null balance, servo-type, 1-millivolt to 10-volt span.

Initial work is planned with Compound R. Purification of this compound will be based on the work reported by Minnesota Mining and Manufacturing Co., using gas chromatographic columns of 33% Kel-F on Celite and 25% perfluorotributylamine dimer on Celite. It is estimated that the purification of 25-cc samples of gas should result in about 0.2g pure sample for shock-tube testing.

The facility will be described in more detail when construction and preliminary operation has been effected.

III. SUMMARY AND CONCLUSIONS

The IITRI cryogenic shock-tube facility has been used in preliminary sensitivity testing of small samples of lead azide in order to check out the equipment procedure and the instrumentation. These preliminary tests have identified some unique results, namely: (1) various levels of light output precede the establishment of a detonation, (2) a fixed level of light output is attained for an erratic induction period before detonation, (3) small amounts of air (believed to be oxygen) decrease the induction times by significant amounts, and (4) the lowering of the initial sample temperature by 200°C decreases the time delay.

Sensitivity is probably best related to the effect of the pressure, temperature, and composition of the driven gas on the induction periods, or time delays, to the establishment of a detonation. These preliminary results have identified at least two induction periods which seem to have different character;

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one is associated with a period of no light output and the other is associated with the appearance of a level of light output which stabilizes at a particular level. The latter period is followed closely by the detonation. The key to sensitivity and desensitization must lie in the identification of the mechanisms that produce this unusual history. Lead azide decompositions have been shown to proceed by different mechanisms, depending upon whether heat or light is the activation source.

The facility to purify samples of the C-N-F compounds is presently being constructed. A gas chromatograph column and a recorder, which have been received, are the basic components for this facility.

IV. FUTURE WORK

Some additional tests are planned with lead azide to further establish the character of shock-tube testing and the results, particularly at cryogenic temperatures. Nitroglycerine is being considered as a supplementary material in order to broaden the experience level. Shock-tube tests will be performed on the purified samples of Compound R as soon as they are available from the chromatographic column; they are expected to be available within a few weeks.

The study and the interpretation of the results of shock-tube tests will be continued; more emphasis will be placed on the steps that are preceding the establishment of the detonation.
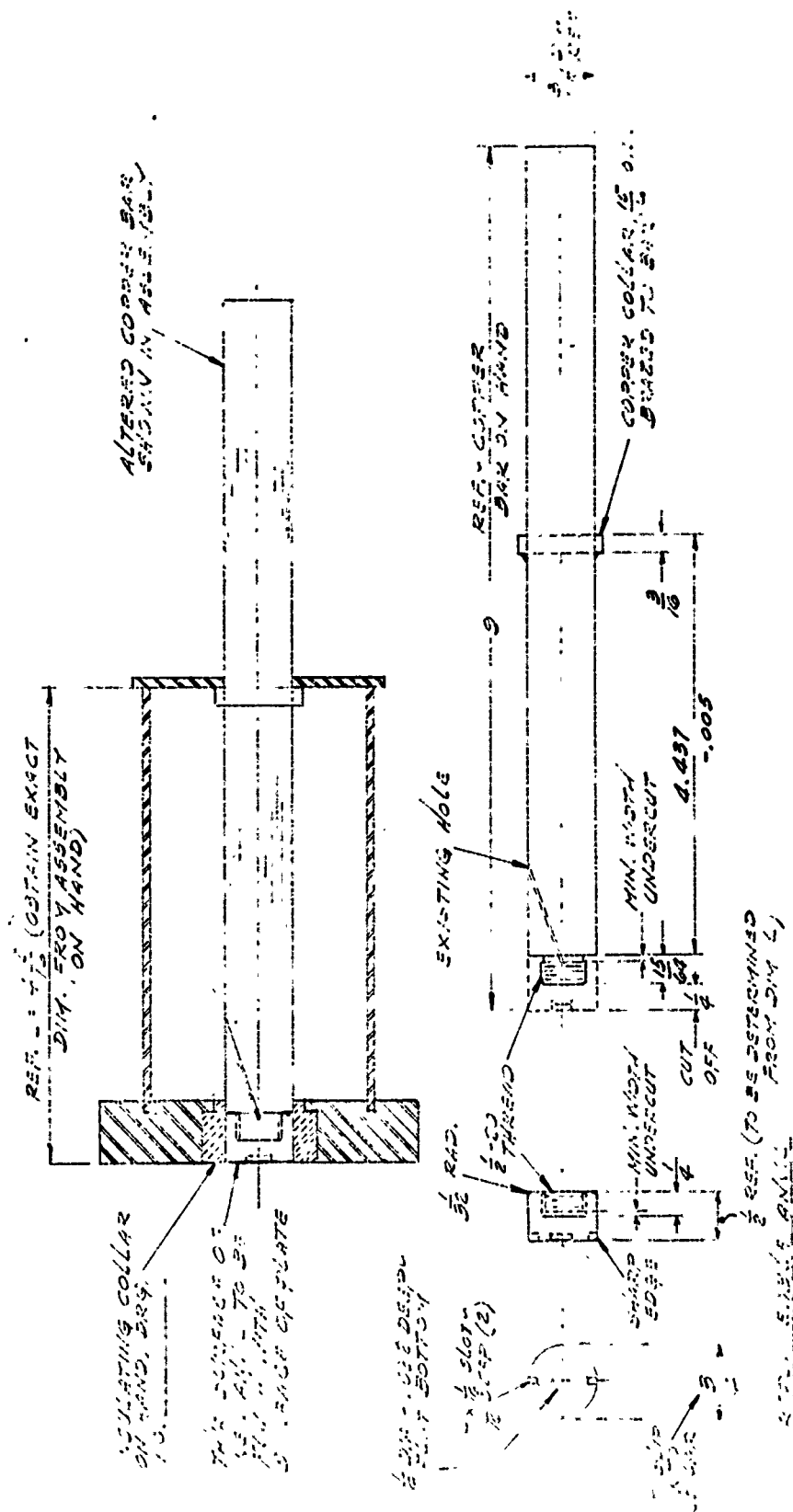
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APPENDIX

HEAT PUMP MODIFICATIONS

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